



Supporting Information

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Supramolecular Catalysis of a Unimolecular Transformation: Aza-Cope
Rearrangement within a Self-Assembled Host**

Dorothea Fiedler, Robert G. Bergman*, Kenneth N. Raymond*

D. Fiedler
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460 (USA)

* Prof. R. G. Bergman
Department of Chemistry
University of California
Berkeley, CA 94720-1460 (USA)
Fax: 510-642-7714
E-mail: bergman@cchem.berkeley.edu

* Prof. K. N. Raymond
Department of Chemistry
University of California
Berkeley, CA 94720-1460 (USA)
Fax: 510-486-5283
E-mail: raymond@socrates.berkeley.edu

Materials and Methods

General Considerations

All reagents were obtained from commercial suppliers and used without further purification unless stated otherwise. Anhydrous solvents were dried over activated alumina. $K_6(NMe_4)_5[NMe_4 \subset Ga_4L_6]$ and *N,N*-dimethylisobutenylamine were prepared according to the published procedures.^[1,2] NMR spectra were measured on Bruker AVB 400 or DRX 500 MHz spectrometers. 1H chemical shifts are reported as δ in ppm relative to residual protonated solvent resonances; ^{13}C chemical shifts are measured relative to solvent resonances. Coupling constants are reported in Hz. IR spectra were recorded on an Avatar 370 FT-IR instrument. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California at Berkeley. Electro Spray mass spectra and FAB spectra were recorded at the University of California, Berkeley, Mass Spectrometry facility; the symbol N^+ denotes the parent ion of the enammonium cation.

Kinetic runs were performed in D_2O on Bruker AVB 400 or DRX 500 MHz spectrometers. The concentration of all samples was 15 mM, and the solutions were buffered with 150 mM phosphate buffer, adjusted to pD 8.00. Sealed capillaries containing a D_2O /dioxane mixture served as internal standard for integration. Temperatures in the probe were measured with an ethylene glycol standard.

Experimental Procedures

General procedure for tosylation reactions:

This is a modified literature procedure:³ In a 500 mL Schlenk flask 15.0 mM of the appropriate allyl alcohol were combined with 80 mL of dry and degassed thf and the solution was cooled to -78 °C. To this solution was added *n*-BuLi (9.34 mL, 15.0 mM, 1.6 M in hexanes). Tosyl chloride (2.86 g, 15.0 mM) was added in a single portion and the homogeneous solution was put in the freezer at -80 °C for 2 days. The reaction was worked up by diluting the reaction mixture at -78 °C with 150 mL of cold petroleum ether. The organic phase was washed with 2 x 50 mL of 50% saturated aqueous NaHCO₃ and 1 x 50 mL of saturated aqueous NaHCO₃. The aqueous layers were combined and extracted with 1 x 50 mL of petroleum ether and the combined organic layers were dried over K₂CO₃. After filtration the volatile materials were removed under reduced pressure, leaving behind the the allyl tosylates as colorless to pale yellow oils in quantitative yields. The tosylates were characterized by ¹H NMR only and used without further purification. The tosylates can be stored in a benzene matrix at -80 °C for several weeks.

Data for allyl tosylates, prepared as described above:

Cis-2-pentenyl tosylate. ¹H NMR (500 MHz, CDCl₃): 7.80 (d, ³*J* = 8.0 Hz, 2H, OTs), 7.34 (d, ³*J* = 8.0 Hz, 2H, OTs), 5.66 (m, 1H, =CH), 5.41 (m, 1H, =CH), 4.60 (d, ³*J* = 7.5 Hz, 2H, OCH₂), 2.45 (s, 3H, OTs), 1.99 (quint., ³*J* = 7.5 Hz, 2H, CH₂), 0.93 (t, ³*J* = 7.5 Hz, 3H, CH₃).

Trans-2-hexenyl tosylate. ^1H NMR (500 MHz, CDCl_3): 7.79 (d, $^3J = 8.0$ Hz, 2H, OTs), 7.34 (d, $^3J = 8.0$ Hz, 2H, OTs), 5.74 (dt, $^3J = 15.5$ Hz, $^3J = 6.5$ Hz, 1H, =CH), 5.45 (dt, $^3J = 15.5$ Hz, $^3J = 7.0$ Hz, 1H, =CH), 4.49 (d, $^3J = 7.0$ Hz, 2H, OCH_2), 2.44 (s, 3H, OTs), 1.97 (m, 2H, CH_2), 1.36 (sext., $^3J = 7.5$ Hz, 2H, CH_2), 0.83 (t, $^3J = 7.5$ Hz, 3H, CH_3).

Cis-2-hexenyl tosylate. ^1H NMR (500 MHz, CDCl_3): 7.79 (d, $^3J = 8.2$ Hz, 2H, OTs), 7.34 (d, $^3J = 8.0$ Hz, 2H, OTs), 5.66 (dt, $^3J = 10.9$ Hz, $^3J = 7.6$ Hz, 1H, =CH), 5.45 (dtt, $^3J = 10.9$ Hz, $^3J = 7.1$ Hz, $^4J = 1.4$ Hz, 1H, =CH), 4.59 (d, $^3J = 7.1$ Hz, 2H, OCH_2), 2.44 (s, 3H, OTs), 1.94 (qd, $^3J = 7.5$ Hz, $^4J = 1.3$ Hz, 2H, CH_2), 1.32 (sext., $^3J = 7.4$ Hz, 2H, CH_2), 0.83 (t, $^3J = 7.4$ Hz, 3H, CH_3) ppm.

4-Methyl-2-trans-pentenyl tosylate. ^1H NMR (500 MHz, C_6D_6): 7.76 (d, $^3J = 8.2$ Hz, 2H, OTs), 6.67 (d, $^3J = 8.0$ Hz, 2H, OTs), 5.32 (dd, $^3J = 15.4$ Hz, $^3J = 6.5$ Hz, 1H, =CH), 5.18 (dtd, $^3J = 15.4$ Hz, $^3J = 6.5$ Hz, $^4J = 1.2$ Hz, 1H, =CH), 4.32 (d, $^3J = 6.6$ Hz, 2H, OCH_2), 1.90 (sext., $^3J = 6.7$ Hz, 1H, *i*-Pr), 1.82 (s, 3H, OTs), 0.70 (d, $^3J = 6.8$ Hz, 6H, *i*-Pr).

General procedure for alkylation reactions:

This is a modified literature procedure:⁴ Under a moisture free atmosphere, a cooled solution (0 °C) of *N,N*-dimethylisobutenylamine (500 μL , 3.76 mmol) in 5 mL of dry acetonitrile was combined with a cooled solution of the appropriate allyl bromide or tosylate (4.14 mmol) in 5 mL acetonitrile *via* cannula. The reaction mixture was stirred at 0 °C for 48 h. All volatile materials were removed under reduced pressure, leading to a

sticky, oily residue. The residue was washed with 5 x 20 mL of dry Et₂O, yielding the analytically pure product.

Data for enammonium salts, prepared as described above:

[NMe₂(allyl)(CH=C(CH₃)₂)]⁺Br⁻ (1). The product was isolated as a very hygroscopic white powder in 94% yield (778 mg, 3.53 mmol). ¹H NMR (500 MHz, CDCl₃): 5.95 (s, br, 1H, =CH), 5.84 (ddt, ³J = 16.9 Hz, ³J = 9.9 Hz, ³J = 7.1 Hz, 1H, =CH), 5.75 (dd, ³J = 16.9 Hz, ²J = 1.2 Hz, 1H, =CH₂), 5.56 (dd, ³J = 9.9 Hz, ²J = 1.3 Hz, 1H, =CH₂), 4.50 (d, ³J = 7.0 Hz, 2H, CH₂), 3.50 (s, 6H, N(CH₃)₂), 1.92 (d, ⁴J = 1.3 Hz, 3H, CH₃), 1.74 (d, ⁴J = 1.3 Hz, 3H, CH₃) ppm. ¹³C{¹H} (125.8 MHz, CDCl₃): 135.2 (=CH), 129.1 (=CH), 128.5 (C_{quart}), 124.8 (=CH₂), 69.3 (CH₂), 54.1 (N(CH₃)₂), 25.3 (CH₃), 19.1 (CH₃) ppm. IR(neat) ν = 3065, 3032, 3013, 2934, 1473, 1462, 1444, 1426, 1404, 1381, 1086, 1023 cm⁻¹. LRFAB-MS (+), *m/z*: 140 [N⁺]. Anal. Calcd. for C₉H₁₈BrN: C, 49.10; H, 8.24; N, 6.36. Found: C, 48.88; H, 8.39; N, 6.12.

[NMe₂(methallyl)(CH=C(CH₃)₂)]⁺Br⁻ (2). The product was isolated as a very hygroscopic white powder in 91% yield (801 mg, 3.42 mmol). ¹H NMR (500 MHz, CDCl₃): 5.98 (s, br, 1H, =CH), 5.47 (d, ²J = 1.3 Hz, 1H, =CH), 5.30 (d, ²J = 1.3 Hz, 1H, =CH), 4.43 (s, 2H, CH₂), 3.48 (s, 6H, N(CH₃)₂), 1.91 (d, ⁴J = 1.4 Hz, 3H, CH₃), 1.77 (s, 3H, CH₃), 1.71 (d, ⁴J = 1.4 Hz, 3H, CH₃) ppm. ¹³C{¹H} (125.8 MHz, CDCl₃): 134.3 (=CH), 133.4 (=CH), 129.5 (C_{quart}), 127.2 (=CH), 72.2 (CH₂), 54.5 (N(CH₃)₂), 25.3 (CH₃), 22.9 (CH₃), 19.1 (CH₃) ppm. IR(neat), ν = 3010, 2971, 2943, 2736, 1643, 1468, 1440, 1418, 1372, 1085, 1006 cm⁻¹. LRFAB-MS (+), *m/z*: 154 [N⁺]. Anal. Calcd. for C₁₀H₂₀BrN: C, 51.29; H, 8.61; N, 5.98. Found: C, 51.02; H, 8.83; N, 5.80.

[NMe₂(*trans*-2-pentenyl)(CH=C(CH₃)₂)]⁺Br⁻ (3). The product was isolated as a hygroscopic colorless oil 95% yield (887 mg, 3.57 mmol). ¹H NMR (500 MHz, CDCl₃): 6.20 (dt, ³J = 15.3 Hz, ³J = 6.4 Hz, 1H, =CH), 5.87 (s, br, 1H, =CH), 5.40 (dt, ³J = 15.3 Hz, ³J = 7.6 Hz, 1H, =CH), 4.39 (d, ³J = 7.4 Hz, 2H, CH₂), 3.44 (s, 6H, N(CH₃)₂), 2.02 (quint., ³J = 7.2 Hz, 2H, CH₂), 1.90 (d, ⁴J = 1.3 Hz, 3H, CH₃), 1.73 (d, ⁴J = 1.3 Hz, 3H, CH₃) ppm. ¹³C{¹H} (125.8 MHz, CDCl₃): 148.1 (=CH), 134.9 (=CH), 128.5 (C_{quart}), 115.3 (=CH), 69.2 (CH₂), 53.7 (N(CH₃)₂), 25.5 (CH₃), 25.3 (CH₂), 19.1 (CH₃), 12.5 (CH₃) ppm. LRFAB-MS (+), *m/z*: 168 [N⁺]. IR(neat) ν = 3010, 2963, 2935, 2874, 1665, 1462, 1453, 1375, 1086 cm⁻¹. Anal. Calcd. for C₁₁H₂₂BrN: C, 53.23; H, 8.93; N, 5.64. Found: C, 52.88; H, 9.23; N, 5.73.

[NMe₂(*cis*-2-pentenyl)(CH=C(CH₃)₂)]⁺OTs⁻ (4). The product was isolated as a white hygroscopic powder in 94% yield (887 mg, 3.57 mmol). ¹H NMR (500 MHz, CDCl₃): 7.73 (d, ³J = 8.1 Hz, 2H, OTs), 7.10 (d, ³J = 7.9 Hz, 2H, OTs), 5.92 (dt, ³J = 10.9 Hz, ³J = 7.7 Hz, 1H, =CH), 5.83 (s, br, 1H, =CH), 5.39 (dt, ³J = 10.9 Hz, ³J = 7.8 Hz, 1H, =CH), 4.31 (d, ³J = 7.7 Hz, 2H, CH₂), 3.44 (s, 6H, N(CH₃)₂), 2.30 (s, 3H, OTs), 2.02 (dq, ³J = 7.6 Hz, ⁴J = 1.3 Hz, 2H, CH₂), 1.91 (d, ⁴J = 1.3 Hz, 3H, CH₃), 1.74 (d, ⁴J = 1.3 Hz, 3H, CH₃), 0.91 (t, ³J = 7.5 Hz, 3H, CH₃) ppm. ¹³C{¹H} (125.8 MHz, CDCl₃): 145.0 (=CH), 143.9 (OTs), 139.0 (OTs), 134.9 (=CH), 128.7 (C_{quart}), 128.5 (OTs), 125.8 (OTs), 115.2 (=CH), 63.9 (CH₂), 53.9 (N(CH₃)₂), 25.5 (OTs), 21.2, 21.1, 18.9, 13.5 (CH₃ and CH₂) ppm. IR(neat) ν = 3028, 2966, 2934, 2872, 1483, 1461, 1205, 1184, 1119,

1032, 1010 cm^{-1} . LRFAB-MS (+), m/z : 168 $[\text{N}^+]$. Anal. Calcd. for $\text{C}_{18}\text{H}_{29}\text{NO}_3\text{S}$: C, 63.68; H, 8.61; N, 4.13. Found: C, 63.50; H, 8.79; N, 4.19.

$[\text{NMe}_2(\text{trans-2-hexenyl})(\text{CH}=\text{C}(\text{CH}_3)_2)]^+\text{OTs}^-$ (5). The product was isolated as a hygroscopic colorless oil in 88% yield (1.12 g, 3.31 mmol). ^1H NMR (500 MHz, CDCl_3): 7.73 (d, $^3J = 8.1$ Hz, 2H, OTs), 7.11 (d, $^3J = 7.9$ Hz, 2H, OTs), 6.06 (dt, $^3J = 15.3$ Hz, $^3J = 6.9$ Hz, 1H, =CH), 5.81 (s, br, 1H, =CH), 5.40 (dt, $^3J = 15.3$ Hz, $^3J = 7.4$ Hz, 1H, =CH), 4.23 (d, $^3J = 7.4$ Hz, 2H, CH_2), 3.39 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.30 (s, 3H, OTs), 2.02 (quart., $^3J = 7.0$ Hz, 2H, CH_2), 1.90 (d, $^4J = 1.4$ Hz, 3H, CH_3), 1.74 (d, $^4J = 1.4$ Hz, 3H, CH_3), 1.36 (sext., $^3J = 7.4$ Hz, 2H, CH_2), 0.85 (t, $^3J = 7.3$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125.8 MHz, CDCl_3): 146.4 (=CH), 143.9 (OTs), 139.0 (OTs), 134.8 (=CH), 128.7 (C_{quart}), 128.5 (OTs), 125.8 (OTs), 116.7 (=CH), 69.4 (CH_2), 53.7 ($\text{N}(\text{CH}_3)_2$), 34.6 (CH_2), 25.4 (OTs), 21.6, 21.2, 18.9, 13.6 (CH_3 and CH_2) ppm. IR(neat) $\nu = 3030, 2959, 2928, 2871, 1665, 1455, 1378, 1192, 1118, 1033, 1011$ cm^{-1} . LRFAB-MS (+), m/z : 182 $[\text{N}^+]$. Anal. Calcd. for $\text{C}_{19}\text{H}_{31}\text{NO}_3\text{S}$: C, 64.55; H, 8.84; N, 3.96. Found: C, 64.18; H, 9.02; N, 4.16.

$[\text{NMe}_2(\text{cis-2-hexenyl})(\text{CH}=\text{C}(\text{CH}_3)_2)]^+\text{OTs}^-$ (6). The product was isolated as a hygroscopic white powder in 94% yield (1.20 g, 3.53 mmol). ^1H NMR (500 MHz, CDCl_3): 7.76 (d, $^3J = 8.1$ Hz, 2H, OTs), 7.12 (d, $^3J = 7.9$ Hz, 2H, OTs), 5.97 (dt, $^3J = 11.0$ Hz, $^3J = 7.6$ Hz, 1H, =CH), 5.84 (s, br, 1H, =CH), 5.46 (m, 1H, =CH), 4.35 (d, $^3J = 7.7$ Hz, 2H, CH_2), 3.49 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.32 (s, 3H, OTs), 2.13 (dq, $^3J = 7.3$ Hz, $^4J = 1.2$ Hz, 2H, CH_2), 1.95 (d, $^4J = 1.3$ Hz, 3H, CH_3), 1.78 (d, $^4J = 1.3$ Hz, 3H, CH_3), 1.36 (sext., $^3J = 7.3$ Hz, 2H, CH_2), 0.86 (t, $^3J = 7.3$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125.8 MHz, CDCl_3): 143.9 (OTs), 143.5 (=CH), 139.0 (OTs), 135.1 (=CH), 128.8 (C_{quart}), 128.5 (OTs), 125.8

(OTs), 116.0 (=CH), 64.2 (CH₂), 54.1 (N(CH₃)₂), 29.7 (CH₂), 25.5 (OTs), 22.2, 21.2, 18.9, 13.6 (CH₃ and CH₂) ppm. IR(neat) ν = 3023, 2967, 1657, 1493.1458, 1210, 1191, 1118, 1033, 1010 cm⁻¹. LRFAB-MS (+), m/z : 182 [N⁺]. Anal. Calcd. for C₁₉H₃₁NO₃S: C, 64.55; H, 8.84; N, 3.96. Found: C, 64.29; H, 8.97; N, 4.20.

[NMe₂(4-methyl-2-*trans*-pentenyl)(CH=C(CH₃)₂)]⁺OTs⁻ (7). The product was isolated as a hygroscopic white solid in 92% yield (1.17 g, 3.46 mmol). ¹H NMR (500 MHz, CDCl₃): 7.77 (d, ³ J = 8.1 Hz, 2H, OTs), 7.13 (d, ³ J = 7.9 Hz, 2H, OTs), 6.08 (dd, ³ J = 15.3 Hz, ³ J = 6.8 Hz, 1H, =CH), 5.81 (s, br, 1H, =CH), 5.38 (dtd, ³ J = 15.4 Hz, ³ J = 7.6 Hz, ⁴ J = 1.2 Hz, 1H, =CH), 4.30 (d, ³ J = 7.4 Hz, 2H, CH₂), 3.46 (s, 6H, N(CH₃)₂), 2.35 (m, 1H, i-Pr), 2.33 (s, 3H, OTs), 1.95 (d, ⁴ J = 1.3 Hz, 3H, CH₃), 1.79 (d, ⁴ J = 1.4 Hz, 3H, CH₃), 0.98 (d, ³ J = 6.8 Hz, 3H, CH₃) ppm. ¹³C {¹H} (125.8 MHz, CDCl₃): 153.2 (=CH), 143.9 (OTs), 139.0 (OTs), 135.1 (=CH), 128.6 (C_{quart}), 128.5 (OTs), 125.9 (OTs), 113.7 (=CH), 69.7 (CH₂), 53.9 (N(CH₃)₂), 31.4, 25.5 (OTs), 25.5, 21.6, 21.3, 19.0 (CH₃ and CH) ppm. IR(neat) ν = 3027, 2965, 2869, 1494, 1461, 1191, 1120, 1032, 1010 cm⁻¹. LRFAB-MS (+), m/z : 182 [N⁺]. Anal. Calcd. for C₁₉H₃₁NO₃S: C, 64.55; H, 8.84; N, 3.96. Found: C, 64.36; H, 8.99; N, 4.08.

General procedure for encapsulation reactions:

K₆(NMe₄)₅[NMe₄ ⊂ Ga₄L₆] (26.3 mg, 7.50 μmol) and the enammonium salt (7.50 μmol) were combined in a vial and dissolved in 500 μL cold D₂O. The solution was transferred to an NMR tube and the spectrum recorded 5 minutes after dissolution. Due to the

reactive nature of these host-guest complexes, the complexes were only characterized in solution. Representative mass spectrometry data is given for host-guest complex $\text{Na}_{11}[\mathbf{1} \subset \text{Ga}_4\text{L}_6]$. The utilization of Na as the counter ion has the advantage of providing a less complicated isotope pattern, thus leading to better signal intensities.

$\text{K}_5(\text{NMe}_4)_6[\mathbf{1} \subset \text{Ga}_4\text{L}_6]$. ^1H NMR (500 MHz, D_2O): δ 13.50 (s, 12H, N-H), 7.95 (s, br, 12H, Ar-H), 7.77 (s, br, 12H, Ar-H), 7.25 (d, $^3J = 7.9$ Hz, 12H, Ar-H), 7.02 (t, $^3J = 8.0$ Hz, 12H, Ar-H), 6.70 (d, $^3J = 7.2$ Hz, 12H, Ar-H), 6.56 (t, $^3J = 7.7$ Hz, 12H, Ar-H), 3.09 (d, $^3J = 7.2$ Hz, 1H, =CH₂, encaps.), 2.65 (s, 72H, NMe₄, exterior), 2.44 (s, br, 1H, =CH, encaps.), 2.32 (m, 1H, =CH, encaps.), 0.24 (s, 3H, CH₃, encaps.), 0.21 (m, 1H, CH₂, encaps.), 0.05 (m, 1H, CH₂, encaps.), -0.03 (s, 3H, CH₃, encaps.), -0.60 (s, 3H, CH₃, encaps.), -1.08 (s, 3H, CH₃, encaps.) ppm. ES(-)-MS ($\text{H}_2\text{O}/\text{MeOH}$, 50:50) $\diamond = [\text{Ga}_4\text{L}_6]^{12-}$, m/z : 605 [$\text{N}^+ \subset \diamond + 2\text{Na}^+ + 4\text{H}^+$]⁵⁻, 610 [$\text{N}^+ \subset \diamond + 3\text{Na}^+ + 3\text{H}^+$]⁵⁻, 614 [$\text{N}^+ \subset \diamond + 4\text{Na}^+ + 2\text{H}^+$]⁵⁻, 619 [$\text{N}^+ \subset \diamond + 5\text{Na}^+ + 1\text{H}^+$]⁵⁻, 623 [$\text{N}^+ \subset \diamond + 6\text{Na}^+$]⁵⁻, 764 [$\text{N}^+ \subset \diamond + 3\text{Na}^+ + 4\text{H}^+$]⁴⁻, 769 [$\text{N}^+ \subset \diamond + 4\text{Na}^+ + 3\text{H}^+$]⁴⁻, 774 [$\text{N}^+ \subset \diamond + 5\text{Na}^+ + 2\text{H}^+$]⁴⁻, 780 [$\text{N}^+ \subset \diamond + 6\text{Na}^+ + 1\text{H}^+$]⁴⁻, 785 [$\text{N}^+ \subset \diamond + 7\text{Na}^+$]⁴⁻, 1017 [$\text{N}^+ \subset \diamond + 3\text{Na}^+ + 5\text{H}^+$]³⁻, 1024 [$\text{N}^+ \subset \diamond + 4\text{Na}^+ + 4\text{H}^+$]³⁻, 1032 [$\text{N}^+ \subset \diamond + 5\text{Na}^+ + 3\text{H}^+$]³⁻, 1039 [$\text{N}^+ \subset \diamond + 6\text{Na}^+ + 2\text{H}^+$]³⁻, 1046 [$\text{N}^+ \subset \diamond + 7\text{Na}^+ + 1\text{H}^+$]³⁻, 1054 [$\text{N}^+ \subset \diamond + 8\text{Na}^+$]³⁻.

$\text{K}_5(\text{NMe}_4)_6[\mathbf{2} \subset \text{Ga}_4\text{L}_6]$. ^1H NMR (500 MHz, D_2O): δ 13.44 (s, 12H, N-H), 7.90 (s, br, 12H, Ar-H), 7.68 (s, br, 12H, Ar-H), 7.18 (d, $^3J = 8.0$ Hz, 12H, Ar-H), 6.93 (t, $^3J = 7.8$ Hz, 12H, Ar-H), 6.62 (d, $^3J = 7.0$ Hz, 12H, Ar-H), 6.48 (t, $^3J = 7.5$ Hz, 12H, Ar-H), 2.52 (s, 72H, NMe₄, exterior), 2.38 (s, br, 1H, =CH, encaps.), 1.63 (s, br, 1H, =CH,

encaps.), 0.89 (s, br, 1H, =CH, encaps.), 0.34 (s, 3H, CH₃, encaps.), 0.21 (d, ³J = 12.5 Hz, 1H, CH₂, encaps.), 0.08 (d, ³J = 12.5 Hz, 1H, CH₂, encaps.), -0.24 (s, 3H, CH₃, encaps.), -0.48 (s, 3H, CH₃, encaps.), -1.24 (s, 6H, 2 x CH₃, encaps.) ppm.

K₅(NMe₄)₆[3 ⊂ Ga₄L₆]. ¹H NMR (500 MHz, D₂O): δ 13.48 (s, 12H, N-H), 7.91 (s, br, 12H, Ar-H), 7.63 (s, br, 12H, Ar-H), 7.17 (d, ³J = 8.0 Hz, 12H, Ar-H), 6.89 (t, ³J = 7.9 Hz, 12H, Ar-H), 6.61 (d, ³J = 7.5 Hz, 12H, Ar-H), 6.46 (t, ³J = 7.5 Hz, 12H, Ar-H), 2.55 (s, 72H, NMe₄, exterior), 2.31 (m, br, 1H, =CH, encaps.), 1.44 (s, br, 1H, =CH, encaps.), 1.24 (m, br, 1H, =CH, encaps.), 0.58 (s, 3H, CH₃, encaps.), 0.28 (m, br, 1H, CH₂, encaps.), 0.21 (s, 3H, CH₃, encaps.), 0.12 (s, 3H, CH₃, encaps.), -0.17 (m, br, 1H, CH₂, encaps.), -0.52 (m, br, 1H, CH₂, encaps.), -0.67 (m, br, 1H, CH₂, encaps.), -1.17 (t, br, 3H, CH₃), -1.38 (s, 3H, CH₃, encaps.) ppm.

K₅(NMe₄)₆[4 ⊂ Ga₄L₆]. ¹H NMR (500 MHz, D₂O): δ 13.45 (s, 12H, N-H), 7.93 (s, br, 12H, Ar-H), 7.65 (s, br, 12H, Ar-H), 7.18 (d, ³J = 8.0 Hz, 12H, Ar-H), 6.89 (t, ³J = 7.7 Hz, 12H, Ar-H), 6.61 (d, ³J = 7.4 Hz, 12H, Ar-H), 6.47 (t, ³J = 7.5 Hz, 12H, Ar-H), 2.82 (m, br, 1H, =CH, encaps.), 2.56 (s, 72H, NMe₄, exterior), 2.29 (s, br, 1H, =CH, encaps.), 2.19 (m, br, 1H, =CH, encaps.), 0.63 (s, 3H, CH₃, encaps.), 0.26 (m, br, 1H, CH₂, encaps.), 0.04 (m, 2H, CH₂), -0.52 (s, 3H, CH₃, encaps.), -1.13 (s, 3H, CH₃, encaps.), -1.23 (t, br, 3H, CH₃), -1.42 (m, 2H, CH₂, encaps.) ppm.

K₅(NMe₄)₆[5 ⊂ Ga₄L₆]. ¹H NMR (500 MHz, D₂O): δ 13.42 (s, 12H, N-H), 7.88 (s, br, 12H, Ar-H), 7.65 (s, br, 12H, Ar-H), 7.15 (d, ³J = 8.0 Hz, 12H, Ar-H), 6.87 (s, br,

12H, Ar-H), 6.61 (d, $^3J = 7.7$ Hz, 12H, Ar-H), 6.46 (t, $^3J = 7.5$ Hz, 12H, Ar-H), 3.11 (s, br, 1H, =CH, encaps.), 2.54 (s, 72H, NMe₄, exterior), 1.76 (s, br, 1H, =CH, encaps.), 0.90 (s, 3H, CH₃, encaps.), 0.38 (s, 3H, CH₃, encaps.), 0.31 (m, br, 1H, CH₂, encaps.), 0.16 (m, br, 1H, CH₂, encaps.), -0.21 (s, br, 3H, CH₃, encaps.), -0.46 (m, br, 1H, CH₂, encaps.), -0.89 (s, br, 4H, CH₃ and CH₂, encaps.), -1.14 (s, br, 3H, CH₃, encaps.), -1.58 (m, br, 2H, CH₂, encaps.) ppm.

K₅(NMe₄)₆[6 ⊂ Ga₄L₆]. ¹H NMR (500 MHz, D₂O): δ 13.45 (s, 12H, N-H), 8.03 (s, br, 12H, Ar-H), 7.73 (s, br, 12H, Ar-H), 7.26 (s, br, 12H, Ar-H), 6.96 (s, br, 12H, Ar-H), 6.70 (s, br, 12H, Ar-H), 6.57 (s, br, 12H, Ar-H), 3.58 (m, br, 1H, =CH, encaps.), 2.52 (s, 72H, NMe₄, exterior), 2.42 (m, br, 1H, =CH, encaps.), 1.37 (s, br, 1H, =CH, encaps.), 0.79 (s, br, 3H, CH₃, encaps.), 0.61 (s, br, 3H, CH₃, encaps.), 0.42 (m, br, 1H, CH₂, encaps.), 0.14 (m, br, 1H, CH₂, encaps.), -0.33 (s, br, 3H, CH₃, encaps.), -0.95 (s, br, 3H, CH₃, encaps.), -1.11 (s, br, 3H, CH₃, encaps.), -1.37 (m, br, 1H, CH₂, encaps.), -1.42 (m, br, 1H, CH₂, encaps.), -1.53 (m, br, 1H, CH₂, encaps.), -1.64 (m, br, 1H, CH₂, encaps.) ppm.

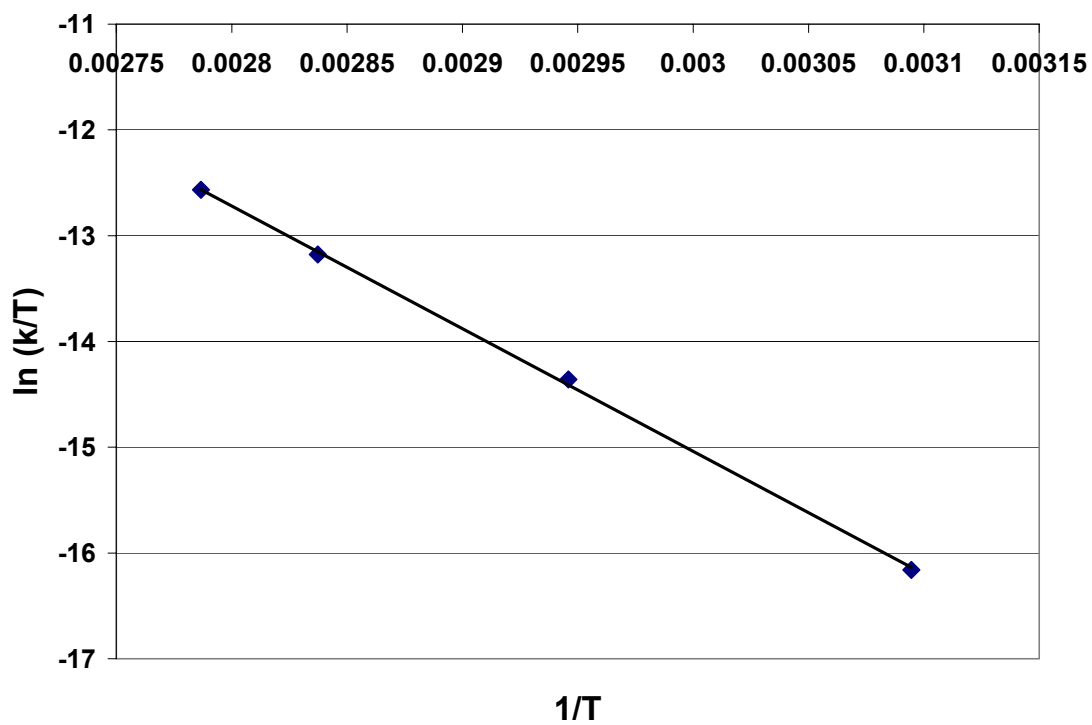
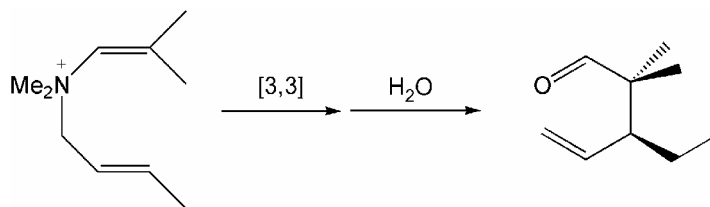
K₅(NMe₄)₆[7 ⊂ Ga₄L₆]. ¹H NMR (500 MHz, D₂O): δ 13.47 (s, 12H, N-H), 8.05 (s, br, 12H, Ar-H), 7.69 (s, br, 12H, Ar-H), 7.26 (s, br, 12H, Ar-H), 6.97 (s, br, 12H, Ar-H), 6.70 (s, br, 12H, Ar-H), 6.56 (s, br, 12H, Ar-H), 2.70 (m, br, 1H, =CH, encaps.), 2.52 (s, 72H, NMe₄, exterior), 1.84 (s, br, 1H, =CH, encaps.), 1.66 (m, br, 1H, =CH, encaps.), 0.93 (s, br, 3H, CH₃, encaps.), 0.85 (s, br, 3H, CH₃, encaps.), 0.69 (m, br, 1H, CH₂, encaps.), 0.49 (s, br, 3H, CH₃, encaps.), -0.42 (m, br, 1H, CH₂, encaps.), -1.32 (s, br, 3H,

CH₃, encaps.), -1.63 (s, br, 3H, CH₃, encaps.), -1.71 (s, br, 3H, CH₃, encaps.), -1.79 (m, br, 1H, CH, encaps.) ppm.

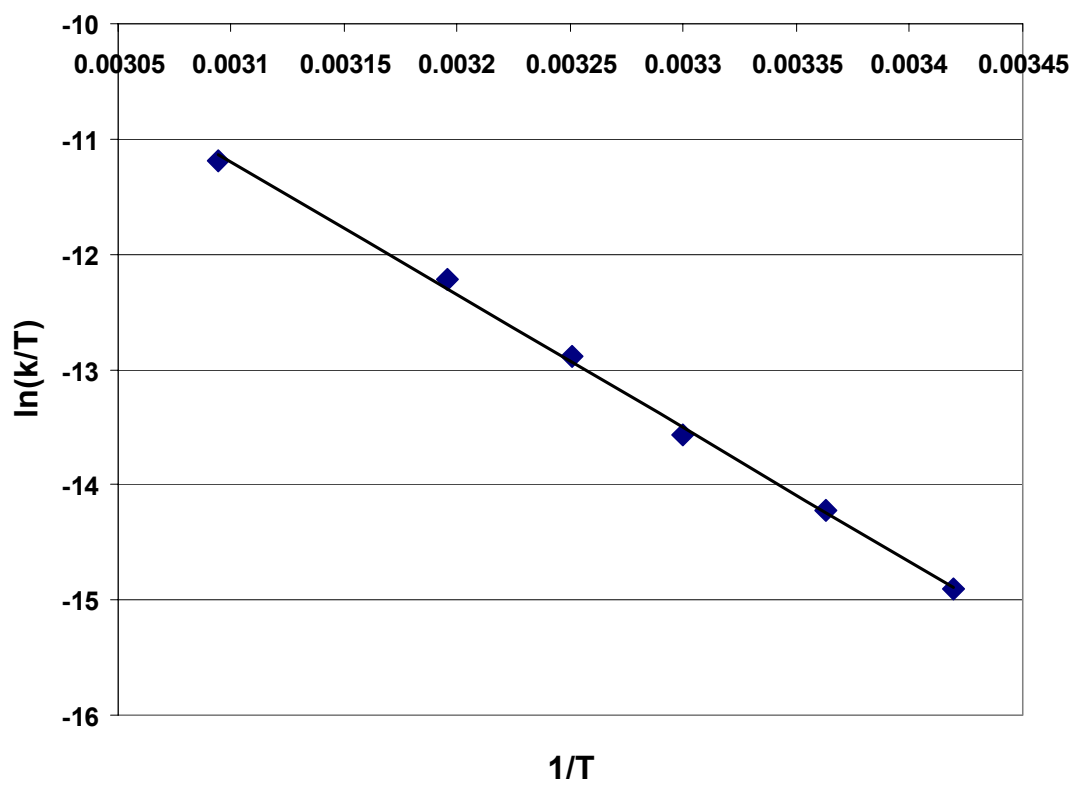
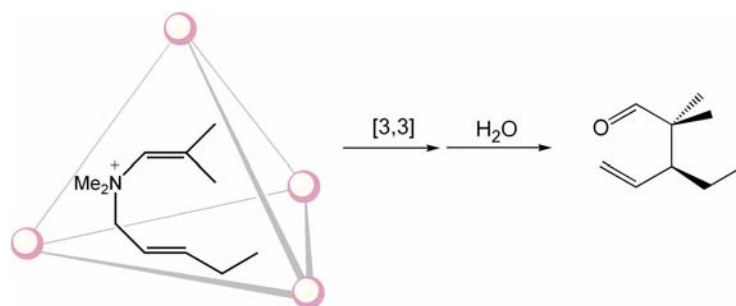
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Eyring Plots

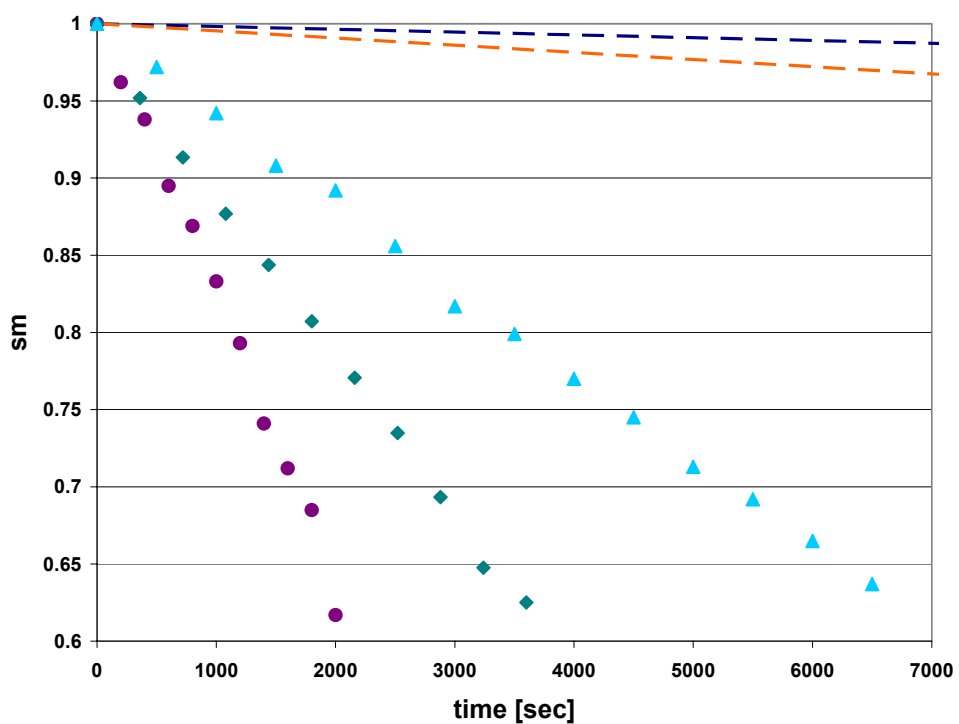
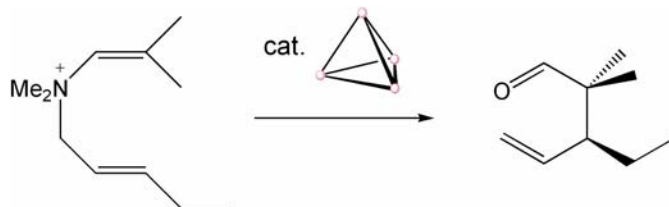


Plot 1. Eyring plot of unencapsulated substrate 3.



Plot 2. Eyring plot of encapsulated substrate 3.

Initial Rates



Initial rates for the catalytic 3-Aza Cope rearrangement. ● = 40% catalyst loading; ◆ = 27% catalyst loading; ▲ = 13% catalyst loading; - - = 40% catalyst loading, inhibited with 8 eq. NEt_4^+ ; - - = uncatalyzed reaction.